Photolysis of fluometuron in the presence of natural water constituents

Sabrina Halladja[1,2], Amina Amine-Khodja[1,2], Alexandra ter Halle[1], Abdelaziz Boulkamh[2] and Claire Richard[1*]

[1]Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR 6505 CNRS-Université Blaise Pascal, Ensemble Universitaire des Cézeaux, F-63177 Aubière CEDEX, France

[2]Laboratoire des Sciences et Technologies de l'Environnement, Université Mentouri, 25000 Constantine, Algérie

[*] corresponding author: Claire Richard

E mail : claire.richard@univ-bpclermont.fr;

tel +33 (0)4 73 40 71 42;

fax : +33 (0)4 73 40 77 00

Abstract. Phototransformation of the herbicide fluometuron (1 µM) in natural sunlight was investigated in neutral Milli-Q water and in synthetic waters containing either fulvic acids, nitrate ions or both in order to mimic reactions taking place in aquatic environments. Fluometuron degradation followed a pseudo-first order kinetics. The reaction was faster in synthetic than in Milli-Q water. Fulvic acids (10 mg L^{-1}) increased the rate of fluometuron photolysis by a factor 2.5 and nitrates (25 mg L^{-1}) by a factor 15. Identification of major photoproducts was conducted under laboratory conditions using LC-ESI-MS. Numerous photoproducts were detected and tentatively characterized. In the presence of nitrates, hydroxylation of the aromatic ring with or without hydrolysis of CF_3 into CO_2H and oxidation of the urea chain leading to demethylation were observed. In the presence of fulvic acids, hydroxylation of the aromatic ring was the major reaction route.

Key-words: phenylurea herbicide, photosensitization, nitrate ions, fulvic acids, hydroxyl radicals

Introduction.

Photochemistry is one of the main route for organic pollutants attenuation in surface waters. This abiotic degradation pathway has received increasing interest in the last thirty years (Zepp and Cline, 1977; Kotzias and Korte, 1981; Durand et al, 1991; Lemaire et al, 1991; Pirisi et al, 1996; Svenson and Hynning, 1997; Mansour et al, 1999). To predict the fate of pollutants in the natural environment and to assess the risk they may pose, it is necessary to improve our knowledge on their chemical reactions.

Several types of reactions may occur depending on the medium composition. Direct photolysis is possible if the considered pollutant absorbs solar light. In addition, photoinduced or photosensitized transformations mediated by components of the aquatic medium can also

take place. In particular, dissolved natural organic matter (DOM) which absorbs a large portion of photons is a potential photosensitizer. Singlet oxygen, superoxide ion/hydroperoxyl radicals, hydroxyl radicals, excited triplet states and alkylperoxyl radicals were proved or proposed to be generated in natural waters under the influence of sunlight (Zafiriou and True, 1979; Zepp et al, 1981; Hoigné et al, 1989; Haag and Hoigné, 1986; Cooper et al, 1989; Vaughan and Blough, 1998; Canonica et al, 1995). However, a part of these species are trapped by DOM itself. Nitrate ions that are present in surface waters at level varying from 0.2 to 25 mg L^{-1} generate the highly oxidizing hydroxyl radicals under light excitation (Boule et al, 1999 for a review). Hydroxyl radicals that are unspecific oxidants are scavenged by a variety of aquatic components. The percentage of hydroxyl radicals trapped by pollutants is thus strongly dependent on the medium composition. Due to all these factors, studies can help to predict the fate of pollutants at the condition that they are undertaken under relevant experimental conditions.

In the present work, we focused on the phototransformation of the phenylurea herbicide fluometuron (FM). This compound is widely used for pre- and post-emergence control of weeds in fields of conventional cotton cultivars. It is persistent (Stoeckel et al, 1997) and may pose some risks to aquatic organisms (Muschal and Warne, 2003). However, literature data are very scarce, especially concerning its photochemical reactivity. FM poorly absorbs solar light (see Figure 1) but indeed its direct photolysis in simulated solar light ($\lambda >$ 290 nm) was reported (Lam et al, 2005). The CF_3 group undergoes photohydrolysis into CO_2H. FM was also included in a recent study (Lam et al, 2003) in which the contribution of indirect processes in surface waters under sunlight simulated irradiation conditions was evaluated. Nitrate ions at a level of $8x10^{-4}$ M significantly enhanced FM degradation while humic acids gave unclear results.

The objective of the present work was to investigate the photolysis of FM in conditions approaching real ones. FM in the micromolar range was irradiated in natural solar light. The influence of DOM or/and nitrates on the phototransformation was assessed. In parallel, laboratories experiments were conducted to identify the main photoproducts on the basis of HPLC-ESI-MS analyses.

Material and Methods

Chemicals. FM (97.7 % purity) was purchased from Riedel de Haën (Saint Quentin Fallavier, France) and used as received. Elliott soil fulvic acids were purchased from International Humic Substances Society (IHSS). The salt used to add nitrate ions was $NaNO_3$ (Fluka, 99 %). All other reactants were of the highest grade available and used as received. Water was purified using a Milli-Q device (Millipore).

Preparation of solutions. A stock solution of FM was prepared by dissolving 4 mg of substrate in 100 ml of Milli-Q purified water. Solubilization was achieved after a 4-day stirring. Stock solutions of fulvic acids and sodium nitrate were prepared in Milli-Q purified water. They were at a concentration of 40 mg L^{-1} and 50 mg L^{-1}, respectively. Stock solutions were then diluted in order to obtain the desired concentrations. Solutions were buffered in order to maintain constant the pH all along irradiations. A pH of 6.5 was chosen because natural aquatic medium is generally around neutrality. Phosphate buffers were used; their final concentration was equal to 10^{-3} M. Deoxygenation of solutions was achieved by nitrogen bubbling for 20 minutes prior to irradiation and during irradiations. Solutions were oxygenated by pure oxygen bubbling.

Photoreaction setup. For kinetic purpose, FM (1 µM) was irradiated (i) in MilliQ water, (ii) in water containing fulvic acids (10 mg L^{-1}) used as a surrogate of DOM, (iii) in water

containing nitrate ions (25 mg L^{-1} or $3x10^{-4}$ M) and (iv) in water containing both fulvic acids (10 mg L^{-1}) and nitrate ions ($3x10^{-4}$ M). Irradiation experiments in natural sunlight were performed at Clermont-Ferrand (46° N, 3° E) in June 2006. Cylindrical quartz glass reactors (14-mm internal diameter) were filled with 14 ml of solutions. A headspace was left above solutions. Reactors were closed by a septum, attached on a rack inclined by about 15° from horizontal and exposed to solar light. Samples received 13 h of sunshine per day. Aliquots of 0.5 mL were removed simultaneously from all the solutions at selected intervals. At each sampling, solutions were re-saturated with air. Samples were immediately analyzed by HPLC. Irradiations started at 9 am on the first day. The first samplings were made at 5 pm. Then, the next samplings were made at 9 am and 5 pm each day. Solutions were left outside overnights. Dark control experiments showed no loss of FM by adsorption on glass surfaces and no transformation, during the time required for the irradiations, irrespective of the aqueous media (variations less than 3 %).

Irradiations under laboratory conditions were also carried out for photoproducts identification. Irradiations were performed in a device equipped with six TLAD 15W/05 fluorescent tubes emitting within the wavelength range 300-450 nm with a maximum of emission at 365 nm and in a Pyrex glass reactor (14 mm i.d). The device was cylindrical and equipped with reflecting inner walls. A ventilator was used as a cooling system. The reactor was placed in the centre of the device and was surrounded by the six fluorescent tubes. Light intensity was measured using *p*-nitroanisole/pyridine as a chemical actinometer (Dulin and Mill, 1982). PNA (10^{-5} M) and pyridine (10^{-4} M) were irradiated in the same conditions as samples in the polychromatic device and in solar light. In the polychromatic device, PNA loss was 12 % after 1 hour and 63 % after 5 h. In solar light, 56 % of PNA had disappeared after 4 h of exposure between 10 am and 2 pm. It can be deduced that the average light intensity

delivered by the tubes of the polychromatic device was of the same magnitude order as that of solar light within the wavelength range 300-400 nm.

Analytical procedures. Loss of fluometuron and formation of photoproducts were monitored by HPLC-UV using a Waters apparatus equipped with two pumps (model 510), an autosampler, a photodiode array detector (model 996), a detector W2487 and a C_{18} reverse-phase column (4.6 mm x 250 mm, Spherisorb S5 ODS2, 5 µm, Waters). Eluent was a mixture of water acidified with 0.1% of orthophosphoric acid and methanol (50 %/50 %) delivered at a constant flow of 1 mL min^{-1}. For the HPLC mass spectrometry analyses, samples containing fulvic acids were prepared as follows. Portions of 0.6 ml of irradiated solutions were passed over an Oasis BHL column conditioned beforehand with 1 ml of methanol and 1 ml of water acidified with formic acid 0.1 %. Fulvic macromolecules were recovered by passing 1 ml of acidified water through the column while fluometuron and its photoproducts by passing 1 ml of methanol. The HPLC-UV-MS analyses were performed using a Waters/Micromass LC/QTOF (Micromass, Manchester,UK). For the HPLC conditions, a Waters Alliance 2695 HPLC equipped with a photodiode array detector (DAD) was used. A reversed-phase column (C18 Hypersil ODS, 5 µm, 100 mm x 2.1 mm; Interchim, Montluçon, France) was used at a flow rate of 0.3 mL min^{-1}. The mobile phase was composed of acetonitrile (solvent A) and acidified water (formic acid, 0.4% v/v; pH 2.6) (solvent B). Gradient: 0-5 min, 5% A; 5–30 min, 5–95% A (linear); 30-34 min, 95% A; 34-35 min, 95-5% A; 35-40 min, 5% B (equilibrium period). The injection volume was 30 µL. The LC-ESI-MS worked both in positive and negative mode. The optimum voltages for the probe and ion source components (to produce maximum intensity) were 3 kV for the stainless-steel capillary, 35 V for the sample cone, and 2 V for the extractor cone. In the negative mode, voltages were switched, except the capillary voltage which was -2.1 kV for better sensitivity. UV spectra were

recorded on a Cary 3 (Varian) spectrophotometer. A 1-cm path quartz cell was used for all the experiments. The reference beam blank was always Milli-Q water.

Results and Discussion

1. Kinetics of phototransformation in solar light

We first compared the profiles of FM loss in various conditions. In the absence of fulvic acids (FA) and nitrate ions, the consumption of FM (1 μM) in solar light was very slow: less than 30 % had disappeared after 6.7 d. The addition of fulvic acids (10 mg L^{-1}) significantly increased the rate of FM consumption: about 50 % of FM had disappeared after 6.7 d. A larger enhancement of the reaction rate was observed in the presence of nitrate ions (25 mg L^{-1}): a complete FM loss was obtained after 3.3 d. In the presence of both fulvic acids (10 mg L^{-1}) and nitrate ions (25 mg L^{-1}), FM disappeared more slowly than in the presence of nitrates alone. To determine rate constants, we plotted $\ln c_0/c$ *vs* irradiation time, where c_0 is the initial FM concentration and c the concentration at t, taking into account that samples were irradiated for 8 h between 9 am and 5 pm and for 5 h between 5 pm and 9 am (Figure 2). In all cases, FM consumption followed pseudo-first order kinetics. The rate coefficients, k, and R^2 values are reported in Table 1.

These kinetic results bring insight into the photodegradability of FM in solar light. FM is hardly transformed in pure water due to the poor absorption of solar radiations. Using the rate coefficient given in Table 1 one computes a half-life of 175 h. This value is 2.6-fold higher than that of Lam et al. (2003). It shows that in the case of FM a one-day irradiation in June in our place is comparable to about 5 h of irradiation in the photosimulator used by these authors.

The chromophoric constituents of water (nitrate and fulvic acids) promoted FM phototransformation. The effect of fulvic acids was quite moderate. In the presence of fulvic

165 acids (10 mg L^{-1}), the rate coefficient was increased by a factor of 2.5 and the half-live
166 reduced by the same factor. Nitrate ions (25 mg L^{-1}) had a more pronounced influence
167 increasing the rate coefficient and reducing the half-live by a factor of 15. In the presence of
168 fulvic acids and nitrate ions, the rate of FM photodegradation was smaller by about 40 % than
169 in the presence of nitrate ions alone. At the considered concentrations, the absorbance of
170 nitrates is very small (around 0.002) while that of FA bigger (around 0.22) for a 1-cm path-
171 length (see Figure 1). The inhibiting effect of FA on nitrate photolysis through screen effect is
172 difficult to evaluate due to the cylindrical shape of reactors. Based on a mean path-length of
173 0.7 cm, one would compute a rate reduction between 15 and 20 %. It represents 50 % of the
174 measured inhibition. The remaining 50 % of inhibition are likely to be due to the scavenging
175 of hydroxyl radicals by FA (Brezonik and Fulkerson-Brekken, 1998; Schindelin and Frimmel,
176 2000, ter Halle and Richard, 2006).

177 In an attempt to delineate the role of hydroxyl radicals in the fulvic acids mediated
178 phototransformation of FM, we studied the influence of 2-propanol added as a hydroxyl
179 radical scavenger on the reaction ($k = 1.9 \times 10^{10}$ M^{-1} s^{-1}, Buxton et al, 1988). These
180 experiments were undertaken in laboratory conditions. In the absence of fulvic acids, the
181 initial rate of FM phototransformation was equal to 2×10^{-8} M h^{-1}. In the presence of fulvic
182 acids (5 mg L^{-1}), it raised to 5.2×10^{-8} M h^{-1}. The addition of 2-propanol (0.015 M) reduced the
183 latter rate by a factor comprised between 1.5 and 2, suggesting the involvement of hydroxyl
184 radicals in the phototransformation reaction and showing the ability of FA to produce them
185 under irradiation. We also studied the influence of oxygen on the reaction. After 5 h of
186 irradiation, FM consumption was twice faster in air-saturated than in oxygen-saturated
187 medium and 3-fold faster in nitrogen-saturated medium than in air-saturated medium. Thus,
188 oxygen clearly inhibited the reaction.
189

2. Photoproducts identification

To achieve photoproducts characterization, we irradiated more highly concentrated FM solutions under laboratory conditions. The photolysis of FM ($3x10^{-5}$ M) in Milli-Q water yielded the acidic compound resulting from the hydrolysis of CF_3 into CO_2H as previously reported (Lam et al, 2005). Its UV absorption spectrum differs from that of FM: the far UV absorption band (λ_{max} = 224 nm) shows a shoulder and the second maximum of absorption is located at 297 nm instead of 275 nm in the case of FM.

The irradiation of FM ($3x10^{-5}$ M) in the presence of fulvic acids (25 mg l^{-1}) yielded two HPLC-UV detectable photoproducts, I and II (Figure 3A). The UV spectrum of I exhibited the same shoulder as that of the acidic product and a second maximum red-shifted by 27 nm (λ_{max} = 297 nm). The UV spectrum of II resembled that of FM but the second maximum was red-shifted by 20 nm compared to it (λ_{max} = 295 nm). The HPLC-mass analysis of I gave a first molecular ion at m/z = 223 in ES^- mode and at m/z = 225 in ES^+ mode corresponding to the loss of 9 amu that may be explained by the hydrolysis of CF_3 into CO_2H and the addition of an oxygen atom. Fragments at m/z = 179 [M-44] and at m/z = 134 [M-89] were obtained in ES^- mode. These data are compatible with the structure proposed in Table 2. The first fragment would correspond to the loss of the carboxylic group and the second to the cleavage of the terminal amine group $-N(CH_3)_2$ followed by loss of an H atom to yield an isocyanate as shown in Scheme 1.

Photoproduct II gave molecular ions at m/z = 247 and 249 in ES^- and ES^+ modes, respectively, corresponding to the addition of an oxygen atom to FM. A fragment at m/z = 202 corresponding to M-45 was observed in ES^- mode. The loss of 45 amu is likely to result from the departure of $N(CH_3)_2$ by cleavage of the terminal urea C-N bond and the elimination of H to form the isocyanate. It is compatible with structure given in Table 2.

214 The irradiation of FM ($3x10^{-5}$ M) in the presence of nitrate ions (25 mg l^{-1}) yielded
215 seven photoproducts detectable by HPLC-UV (see Figure 3 B). Based on HPLC retention
216 times, UV absorption spectra and mass data, we could conclude that photoproducts I and II
217 were present among the seven photoproducts. Two other compounds III and IV with a
218 molecular ion at m/z = 223 in ES^- mode were also detected. As they showed distinct retention
219 times and UV maxima, but similar fragmentation at m/z =179 and 134 with different
220 percentages of fragments, they are likely to be isomers of I. Photoproducts I, III and IV
221 should differ from each other in the position of the hydroxyl group on the ring. The
222 photoproducts V and VI that were eluted just before FM showed similar absorption spectra.
223 One of them, V, gave a molecular ion at m/z = 203 in ES^- mode corresponding to the loss of
224 28 amu and a fragment at m/z = 160. The other one, VI, gave a molecular ion at m/z = 217 in
225 ES^- mode and the same fragment at m/z = 160 (see Scheme 2). These compounds could be
226 assigned to demethylated products; VI would be the monodemethylated derivative and V the
227 didemethylated derivative (see Table 2).

228 A molecular ion at m/z = 245 in ES^- mode was also detected at a retention time longer
229 than that of FM. This mass corresponds to the addition of 14 amu. Three fragments were
230 observed at m/z = 217 [M-28], 188 [M-28-29] and 160 [M-28-29-28]. This fragmentation
231 indicates that the aromatic ring was not altered. It is in favour of photoproduct VII that bears a
232 carbonyl group and for which successive losses of CO, NCH_3 and CO are again possible.

233 Finally, we used the selected peak method to detect some specific photoproducts
234 formation of which was expected. In the case of nitrate ions, we could find nitro derivatives at
235 m/z = 276 in ES^- mode corresponding to the addition of 45 amu ($+NO_2$-H). In the case of
236 fulvic acids, careful examination of chromatograms revealed the presence of peaks at m/z =
237 217 and 245 in ES^- mode and m/z = 219 in ES^+ mode, showing that fulvic acids

photosensitized transformation also yielded FM demethylation, but this pathway was very minor.

3. Mechanisms of reactions

FA and nitrates both accelerated the phototransformation of FM through different reaction mechanisms. Nitrate absorbs solar radiation in the actinic spectrum (ε_{304} = 7.4 M^{-1} cm^{-1}) and produces photoreactants through the two following primary processes (Boule et al, 1999) :

$NO_3^- + h\nu \rightarrow NO_2^- + O$

$NO_3^- + h\nu \rightarrow NO_2^{\bullet} + O^{-\bullet}$

$O^{-\bullet} + H^+ \leftrightarrow HO^{\bullet}$

The formation of hydroxyl radicals is 9-fold more efficient than that of atomic oxygen. As hydroxyl radicals are also much stronger oxidants than atomic oxygen, they are generally considered to be the main species involved in the nitrate-photoinduced transformations of organic compounds, even though nitration reactions were also reported to occur (Machado and Boule, 1994; Vione et al., 2001). Hydroxylation of the aromatic ring and oxidation/elimination of the methyl groups of the urea aliphatic chain confirm that FM was oxidized by hydroxyl radicals (Scheme 3).

The aromatic ring of FM is a site of attack for hydroxyl radicals. The OH-adduct radical is expected to yield the ring hydroxylated compound (photoproduct II). Photoproducts I, III and IV are also ring hydroxylated products, but, contrary to II, they bear the CO_2H substituent instead of the CF_3 substituent initially present in FM. The formation of these products requires two steps. Either they are produced by photohydroxylation of the acid, or they result from the direct photolysis of photoproduct II. Photoproduct II which shows a maximum of absorption at 295 nm instead of 275 nm for FM absorbs solar light better than

263 FM, and thus could undergo faster photolysis. In both cases, several isomers corresponding to
264 the possible sites of attack for hydroxyl radicals are expected. As three hydroxylated acids
265 were detected, three hydroxylated derivatives of FM should be produced too. We only
266 detected one peak at the mass m/z = 247 in ES^-. Either, the three isomers show the same
267 retention time and are eluted altogether, or we have failed to detect two of them.

268 The second site of attack of hydroxyl radicals is the urea aliphatic chain. Three
269 photoproducts were detected: the carbonyl derivative VII, the monodemethylated product VI
270 and the didemethylated product V. The first step should be the abstraction of a H atom from
271 CH_3 to form the $CH_2^{\bullet}$ radical that can add oxygen and finally give V, VI and VII. On the
272 HPLC chromatograms and by total ion count (TIC), the area of products V, VI and VII were
273 higher than those of products I-IV. It seems therefore that the attack of the urea terminal chain
274 is the main reaction pathway. However, without titration of photoproduct to measure chemical
275 yields, this argument must be taken with caution because ring hydroxylation and hydrolysis of
276 CF_3 significantly shift maxima of absorption to longer wavelengths and photoproducts I-IV
277 might not accumulate due to photoreactivity. In the chromatograms of solar-light irradiated
278 solutions of micromolar FM, only photoproducts VI and VII were detectable.

279 Fulvic acids are known to produce several photoreactants under light excitation
280 (oxidant excited states, singlet oxygen, radicals). The quite small photosensitizing effect of
281 fulvic acids on FM shows that FM is not easily oxidized by these species. A part of the
282 reaction can be attributed to hydroxyl radicals as confirmed by the detection of product VI as
283 a minor by-product and the inhibiting effect of 2-propanol on the reaction. The two main
284 photoproducts were I and II. Contrary to what was observed in the nitrate-mediated
285 phototransformation, only one hydroxylated acid derivative was produced in the presence of
286 fulvic acids. This result suggests that the FA mediated ring hydroxylation does not involve
287 hydroxyl radicals. As an alternative, the hydroxylation reaction could involve the triplet

288 excited state of FA ($^3FA^*$). $^3FA^*$ reacts with FM either through energy transfer or through
289 electron transfer. We found that the rate of FM phototransformation is accelerated upon
290 deoxygenation of the medium by nitrogen bubbling as in the case of monuron (Richard et al,
291 1997). This result confirms the involvement of $^3FA^*$ in FM photodegradation but does not
292 clear up the mechanism. In the case where an energy transfer reaction would occur, $^3FM^*$
293 would be produced. Oxidation photoproducts are formed. It implies that $^3FM^*$ is oxidized. As
294 direct photolysis of FM leads to acidification of CF_3 substituent, one would conclude that
295 singlet and triplet excited states of FM react differently. As an alternative, electron transfer
296 from FM to $^3FA^*$ could occur. It is the hypothesis proposed by Gerecke et al (2001). This
297 hypothesis was also adopted in the case of fenuron, an analog of FM, because the FA
298 mediated phototransformation of fenuron was found to be inhibited by removal of oxygen
299 (Richard et al, 1997). Thus, the mechanism of reaction of FM is not clear. Further addition of
300 dioxygen on the ring should finally produce the hydroxylated products, either photoproduct II
301 in the case where the oxidation step involves FM or photoproduct I if it involves the acid, the
302 photoproduct of direct photolysis. As proposed above, II might also produce I by photolysis.
303
304 **Conclusion**
305 In conclusion, direct photolysis of aqueous FM is slow but photosensitizing processes
306 may promote its transformation in surface waters. In the presence of hydroxyl radicals, both
307 the lateral chain and the ring of FM are oxidized. Photoreactants deriving from fulvic acids
308 privilege oxidation of the aromatic ring. Photoproducts of hydrolysis or hydroxylation of the
309 aromatic ring absorb solar light better than FM itself. They are thus susceptible to undergo
310 photolysis faster than FM. Photoproducts resulting from oxidation of lateral urea chain are
311 more photostable. It would be now necessary to test the toxicity of each individual compound

312 or that of the irradiated mixtures toward reference organisms in order to access the risk that
313 may pose FM.
314

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Captions for figures

Figure 1 : Absorption spectrum of (----) FM at $3x10^{-4}$ M, (—) FA at 10 mg L^{-1}, (···) nitrates at 0.01 M and solar light emission reaching the earth surface in summer from Zepp and Cline, 1977.

Figure 2 : Kinetics of FM (10^{-6} M) phototransformation in solar light in various aqueous media. Plot of $\ln c_0/c$ *vs* the irradiation time, where c and c_0 were the concentrations at t and t=0, respectively.

■ : in pH 6.5 MilliQ purified water

● : in water containing FA (10 mg L^{-1})

▲ : in water containing FA (10 mg L^{-1}) and nitrates (3.10^{-4} M)

▽ : in water containing nitrates (3.10^{-4} M)

Figure 3 : HPLC chromatogram of (A) a neutral solution of FM ($3x10^{-5}$ M) containing fulvic acids (25 mg L^{-1}) at a conversion extent of 20 % and (B) a neutral solution of FM ($3x10^{-5}$ M) containing nitrate ions (25 mg L^{-1}) at a conversion extent of 46 %. Both solutions were irradiated in simulated solar light. Photoproducts are numbered as indicated in Table 2.

439 Table 1 : Phototransformation of FM (10^{-6} M) in solar light. Rate coefficients deduced from
440 logarithmic decay, correlation values and half-lives considering that samples were irradiated
441 for 13 h per day.
442

Conditions	k (s^{-1})	R^2	$t_{1/2}$ (h)
FM in MilliQ water, buffered at pH 6.5	1.1×10^{-6}	0.972	175
FM in presence of FA (10 mg L^{-1})	2.7×10^{-6}	0.983	71
FM in presence of nitrate ions (25 mg L^{-1})	1.7×10^{-5}	0.991	11
FM in presence of FA (10 mg L^{-1}) and nitrate ions (25 mg L^{-1})	1.1×10^{-5}	0.986	18

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451 Table 2 : Proposed structure of detected photoproducts, retention time in HPLC-UV,

452 maxima of absorption, molecular ions and main fragments detected by LC-ESI-MS.

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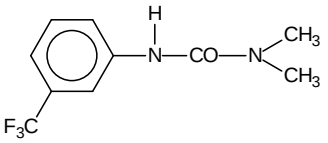
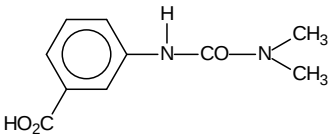
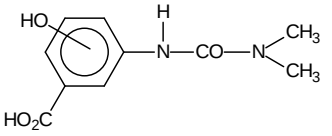
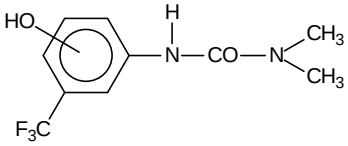
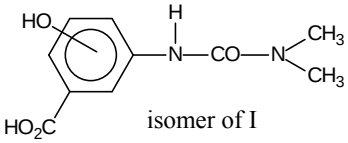
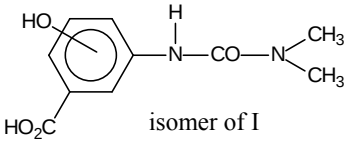
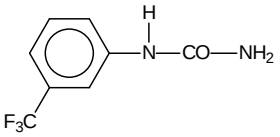
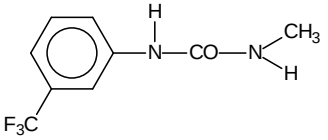
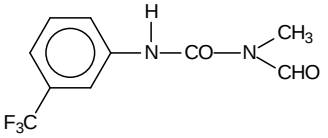
formula	number	Molecular weight	Condition of obtention	λ_{max} (nm)	m/z and main fragments (%)
	FM	232		242/275	ES^- : 231
	acid	208	Pure water	224/297	ES^- : 207
	I	224	FA or nitrates	222/324	ES^- : 223 (179, 134) ES^+ : 225
	II	248	FA or nitrates	242/295	ES^- : 247 (202) ES^+ : 249
 isomer of I	III	224	Nitrates	230/311	ES^- : 223 (179, 134)
 isomer of I	IV	224	Nitrates	224/315	ES^- : 223 (179, 134)
	V	204	Nitrates	241/280	ES^- : 203 (160)
	VI	218	Nitrates or FA (minor)	243/279	ES^- : 217 (160)
	VII	246	Nitrates	245 and shoulder at 280	ES^- : 245 (217, 188, 160)

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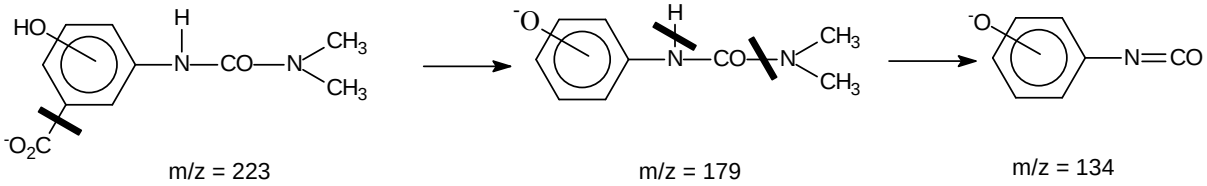
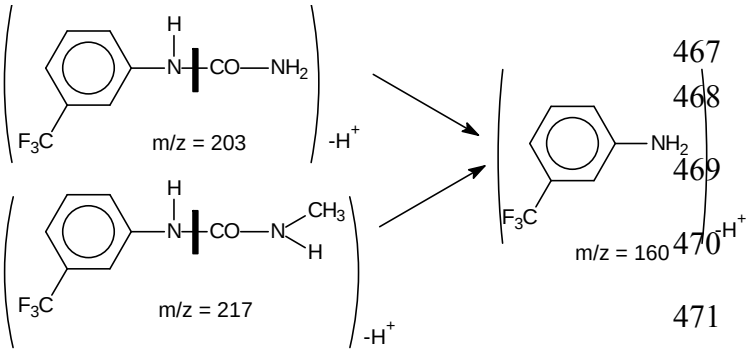


Scheme 1: Fragmentation of photoproduct I



Scheme 2: Fragmentation of photoproducts V and VI

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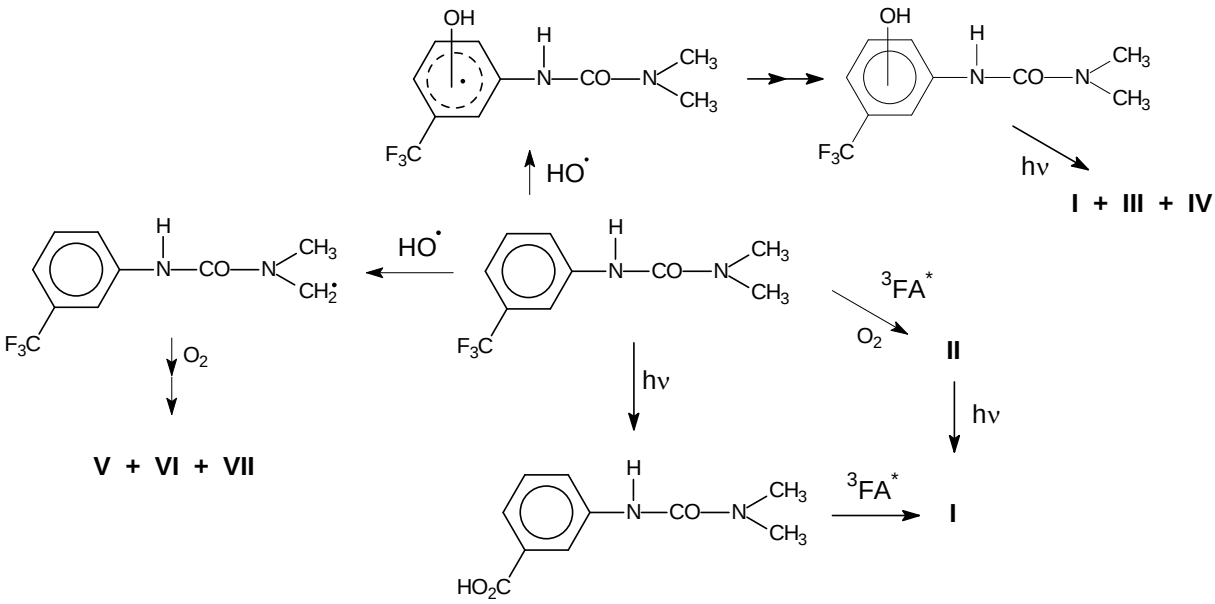

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481 Scheme 3: Proposed reaction scheme

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Figure 1

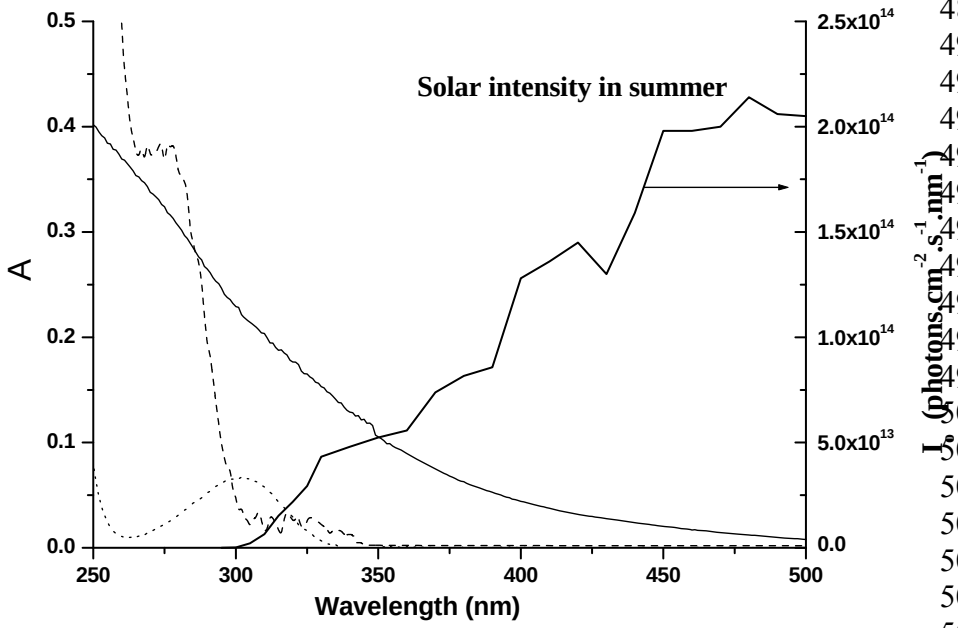


Figure 2

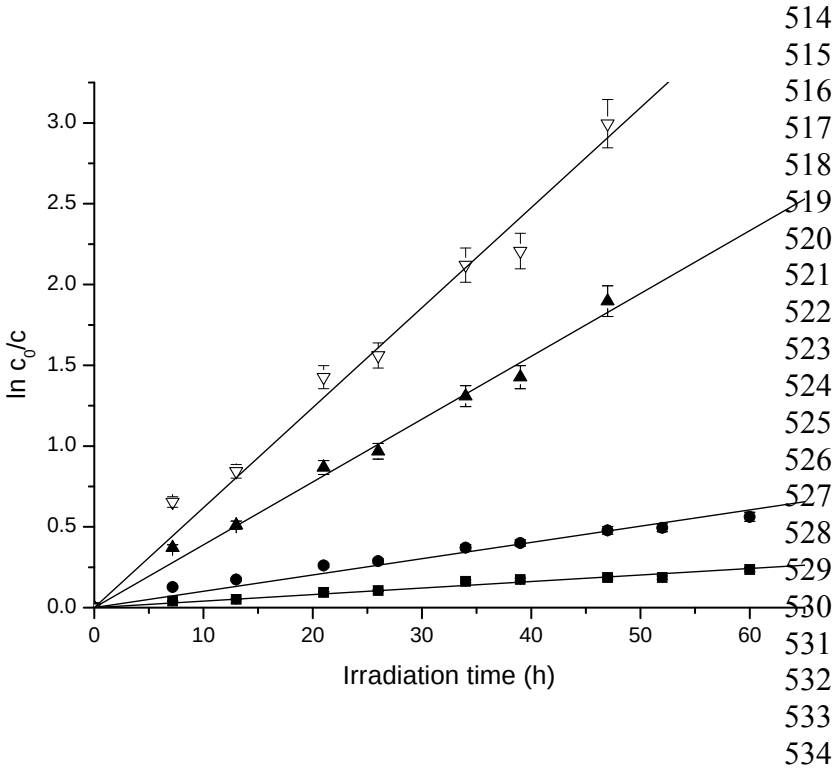
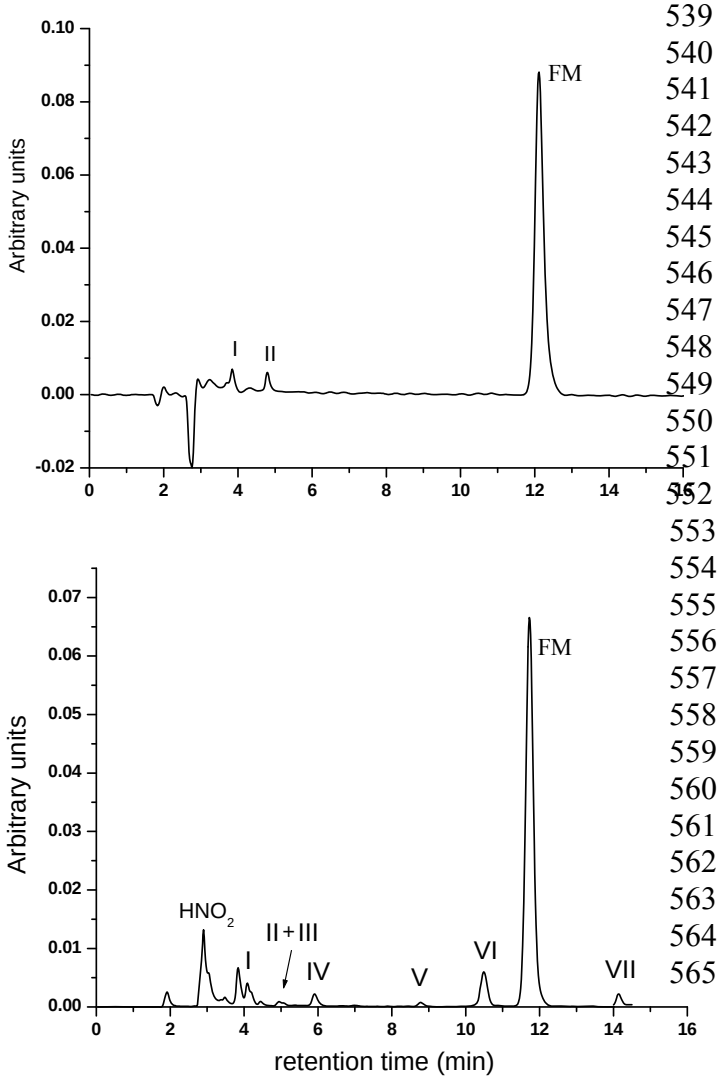


Figure 3


A
Arbitrary units
FM
I
II
B
Arbitrary units
HNO2
I
II + III
IV
V
VI
VII
FM
retention time (min)